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Chemical Analysis of Hydrocarbon Grease from Spin Bearing Tests

R. BAUER, D. J. CARRÉ, and P. D. FLEISCHAUER
Chemistry and Physics Laboratory
The Aerospace Corporation
El Segundo, Calif. 90245

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Steven G. Hancock

Steven G. Hancock, 2nd Lt, USAF
Project Officer

Jimmie H. Butler

Jimmie H. Butler, Colonel, USAF
Director of Space Systems Technology

FOR THE COMMANDER

Norman W. Lee

Norman W. Lee, Jr., Col USAF
Deputy for Technology

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The rotor bearing drag torque levels of certain spin bearing units were found to increase significantly during extended life testing. Samples of the greases from these tests were analyzed to determine if lubricant degradation was linked with the increased torque levels. By means of chromatographic and spectroscopic techniques, we were able to determine that oxidation of some of the greases had occurred and that the oxidative degradation was most easily observed in the soap thickener portion of the grease. A correlation between

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unsaturated fatty acid salt degradation and torque levels was observed, i.e., the grease sample with the highest torque level history suffered the most oxidative degradation. Polymerization of the greases was observed in all samples and appeared to be independent of oxidation. We also determined that the grease degradation was a symptom of adverse mechanical conditions in the bearings and not the primary cause of mechanical problems.

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1. INTRODUCTION

To meet their mission requirements, current and future satellites must operate in orbit for extended periods of time. The satellite subsystems and components, therefore, are required to operate trouble-free during the mission lifetime. Bearings and their associated lubricants are ubiquitous in satellite systems and, as components, must meet these requirements.

During a series of accelerated and extended life tests, certain spin bearing units exhibited increased drag torque levels. When the units were disassembled, the lubricant appeared to be degraded. As a result, chemical analysis of the lubricant, a specially formulated naphthenic oil-sodium soap thickened grease, was undertaken in an attempt to determine whether lubricant failure was the sole cause of the increased drag torque levels or a symptom of adverse mechanical conditions in the bearing.

The work reported herein includes a discussion of the chemical analysis of the grease and hypotheses and conclusions pertaining to the chemistry of lubricant oxidation and polymerization.

2. EXPERIMENTAL

A. LUBRICANT

The lubricant employed in the tests was a specially formulated naphthenic oil based-sodium soap thickened grease.

B. TEST CONDITIONS

The lubricant was run in bearings under two test conditions: life tests (LT) and accelerated tests (AT). The test parameters are given in Table 1.

C. VISUAL ANALYSIS

The greases from the LT and AT tests appeared to be in various stages of degradation. All the samples contained dark particles, and the color of the samples varied from light tan (like the unused grease) to very dark.

The bearings were examined following the tests, and the cross curvature deviations for the bearings from LT No. 1 and LT No. 5 were found to be significantly larger than those for the other tests.

D. SEPARATION OF SAMPLES

The grease samples were received and the components were separated according to the scheme shown in Fig. 1, in which the oil portion of the grease was extracted into heptane and subsequently analyzed. The solid residue, containing the soap thickener, was refluxed with HCl (15%)/CH_3OH to convert the soap molecules to methyl esters. The esters were extracted into heptane and analyzed. The remaining residue, primarily particulate material, was also analyzed. The samples are identified in Table 2.

E. ANALYTICAL METHODS

The unseparated grease was first subjected to infrared spectrophotometric analysis by means of a Perkin Elmer Model 467 infrared spectrophotometer. Infrared spectrometry was also used to analyze the separated grease components. Unseparated grease samples were sent to Pacific Spectrochemical Laboratory Inc. for emission spectrographic analysis.

Table 1. Test Operating Parameters

	LT 1	LT 3	LT 4	LT 5	LT 6	AT 2
Bearing Temp (°C)	42–47	39–46	39–46	42–47	39–46	55–63
Test Pressure (torr)	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-3}
Life (hr)	15K	50K	50K	9K	50K	> 3K
Bearing Type and Size	ABEC 7 304H	ABEC 7 304H	ABEC 7 304H	ABEC 7 304H	ABEC 7 304H	ABEC 7 304H

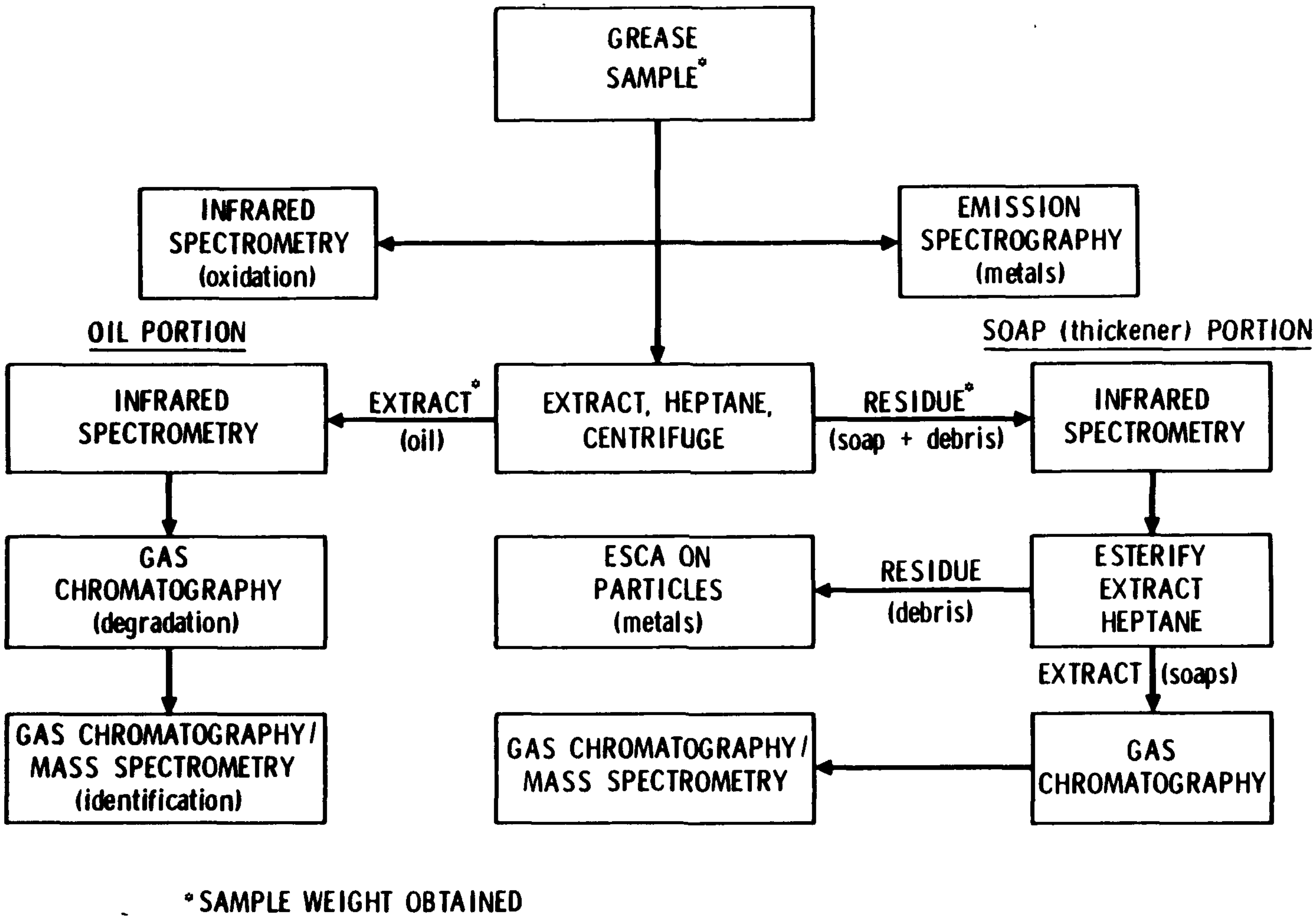

Fig. 1. Grease Sample Analysis

Table 2. Identification of Grease Samples

Sample	Identification
1	Unused Grease (Same batch as used in tests)
2	AT 2 - Bearing B
3	LT 4 - Bearing B
4	LT 1 - Bearing A
5	LT 1 - Bearing A
6	LT 1 - Bearing B
7	LT 3 - Bearing A
8	LT 3 - Bearing B
9	AT 2 - Bearing B
10	AT 2 - Bearing B
11	AT 2 - Bearing A
12	LT 4 - Bearing A
12A	LT 4 - Bearing A
13	LT 6 - Bearing A
13A	LT 6 - Bearing A
14	LT 6 - Bearing B
14A	LT 6 - Bearing B
17	LT 5 - Bearing A
18	LT 5 - Bearing B

The separated oil and soap methyl ester portions were analyzed by means of a Hewlett-Packard Model 5840A gas chromatograph (GC) equipped with an OV-101 capillary column and a flame ionization detector. The instrument was used in the temperature programmed mode over the temperature range 175 to 250°C. Retention times (RT) remained constant within 2% from run to run.

A Finnigan 3200 gas chromatograph mass spectrometer (GC-MS) was used to identify components separated on the gas chromatograph. In the GC column, OV-1 was used as the active phase with hydrogen as the carrier gas. The same temperature programming was used for the GC and GC-MS analyses. To obtain better molecular weight information, the instrument was also operated in the chemical ionization mode with methane used as the carrier gas.

The particulate material was analyzed using a McPherson ESCA 36 X-ray photoelectron spectrometer (XPS). XPS analysis gives only surface analysis to a depth of approximately 40 Å and a sensitivity of approximately 1%. In addition, the particles were examined microscopically at 10 to 100X.

3. RESULTS

A. EMISSION SPECTROGRAPHIC ANALYSIS

The results of the emission spectrographic analysis are given in Table 3. Samples corresponding to LT No. 5 were not analyzed because of the small sample size. The data clearly show enhanced levels of iron and chromium for samples 4 and 6 (both LT No. 1) indicating that bearing wear or chemical reaction between the lubricant and the bearing was more significant in LT No. 1 than in the other tests. Samples 2, 9, and 11 (AT No. 2) exhibited elevated levels of nickel, probably because the shaft in the accelerated test was of a high-nickel content maraging steel, which apparently contaminated the grease upon disassembly.

B. INFRARED SPECTRAL ANALYSIS

The infrared spectra of the unused grease and the AT No. 2 samples are qualitatively identical. The spectra for the LT samples all exhibit absorption bands centered at approximately 3400 cm^{-1} (hydroxyl) and 1700 cm^{-1} (carbonyl), which indicate oxidation. The carbonyl band is present in both the oil and soap fractions, indicating that ketones, aldehydes, and carboxylic acids are oxidation possibilities. The hydroxyl absorption is absent from the oil spectrum but is present in the analysis fraction that contains the soap portion of the grease. The hydroxyl groups are probably the result of oxidation of the soap molecules. The 3400 cm^{-1} absorption could also be caused, in part, by water. However, treatment of one of the methyl ester solutions with the drying agent $CaSO_4$ did not significantly reduce the 3400 cm^{-1} absorption. Thus, the contribution of water to the hydroxyl absorption in the infrared must be small. Representative spectra are shown in Figs. 2 and 3.

C. GAS CHROMATOGRAPHY

Typical gas chromatograms of the oil portion and the esterified fatty acids (soap portions) are shown in Figs. 4 through 6. The GC trace for the oil portion of the unused grease, Fig. 4, exhibits a sharp peak at RT = 10.31 min followed by an envelope. The sharp peak corresponds to the antioxidant

Table 3. Emission Spectrograph Results for Grease Samples[a]

Sample	Identification	Sodium	Iron	Chromium	Nickel
1	unused	2.4	0.0079	0.00085	<0.00005
2	AT 2-Bearing B	3.0	0.050	0.0018	0.002
3	LT 4-Bearing B	2.8	0.0073	0.0071	0.00017
4	LT 1-Bearing A	3.2	0.14	0.025	0.00019
6	LT 1-Bearing B	3.5	0.10	0.016	0.00019
7	LT 3-Bearing A	2.9	0.034	0.0064	0.00013
8	LT 3-Bearing B	3.4	0.032	0.0083	0.00032
9	AT 2-Bearing B	3.6	0.024	0.0064	0.0011
11	AT 2-Bearing A	3.0	0.045	0.0041	0.00060
12	LT 4-Bearing A	3.1	0.028	0.0070	0.00045
13	LT 6-Bearing A	2.7	0.013	0.0041	0.00021
14	LT 6-Bearing B	2.7	0.026	0.0085	0.00028

[a]Values in weight percent

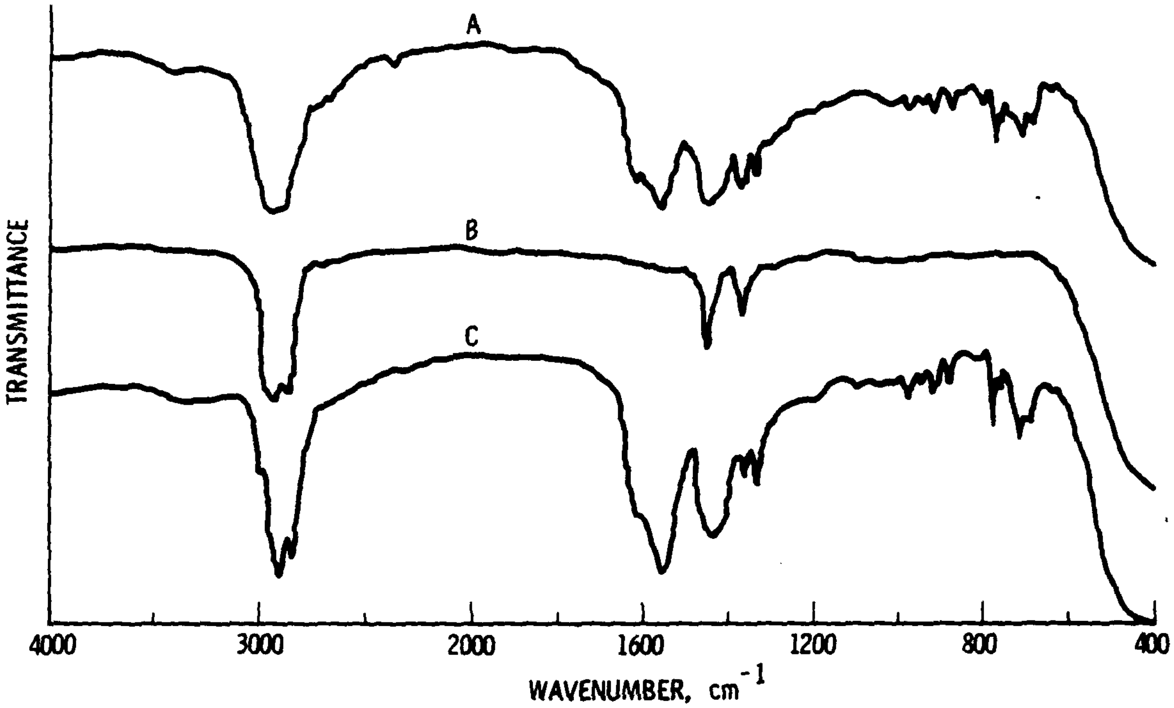

Fig. 2. Typical Infrared Spectra of Unused Grease Components. (A) Unseparated Grease; (B) Oil Portion; (C) Soap Portion

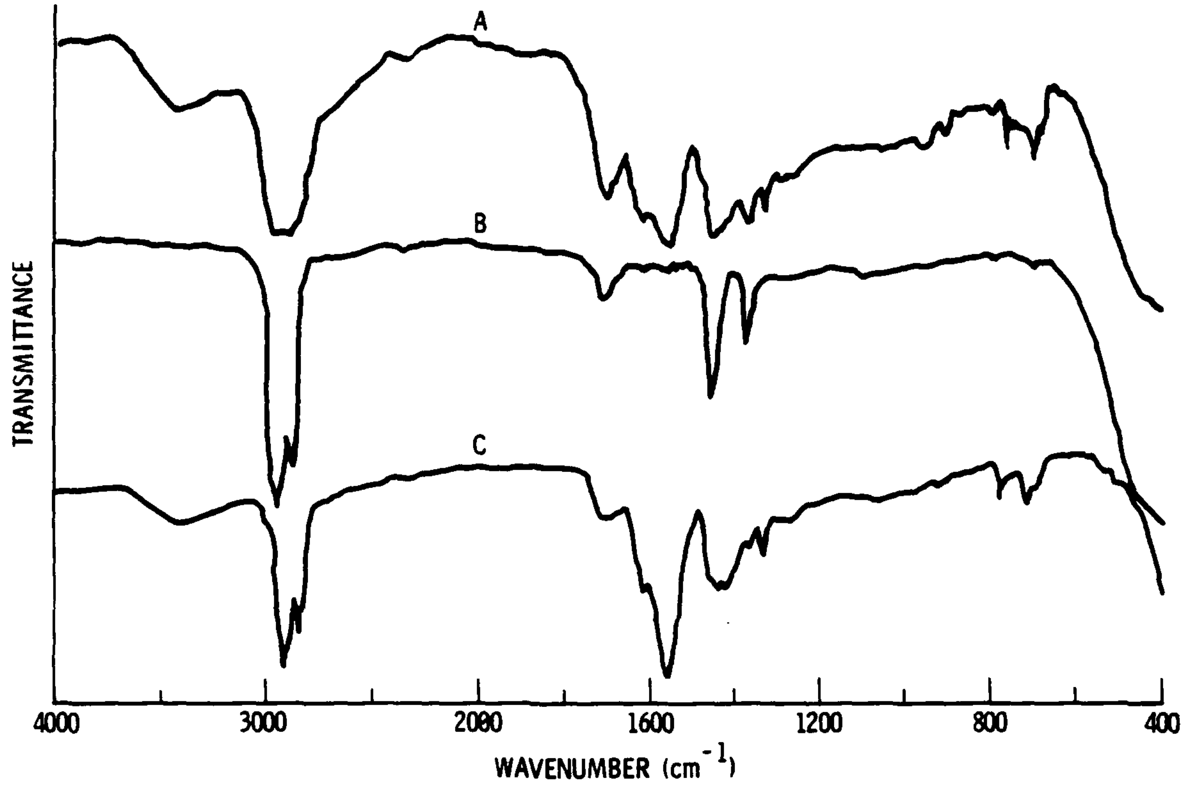

Fig. 3. Typical Infrared Spectra of Life Test Grease Components. (A) Unseparated Grease, LT 3; (B) Oil Portion, LT 3; (C) Soap Portion, LT 4

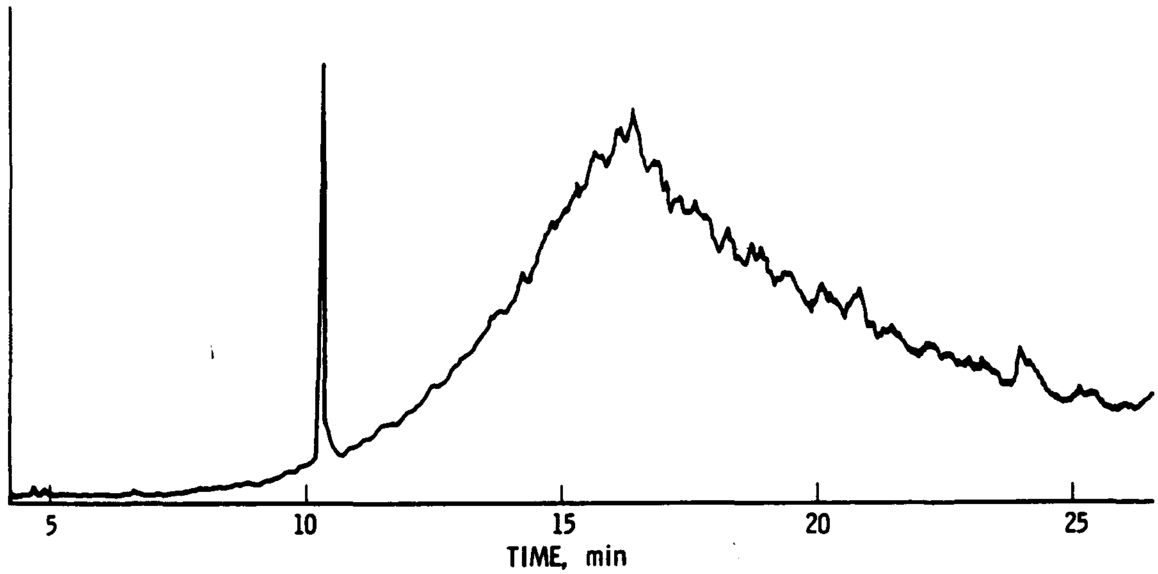

Fig. 4. Gas Chromatogram of Unused Grease-Oil Portion in Heptane Solvent

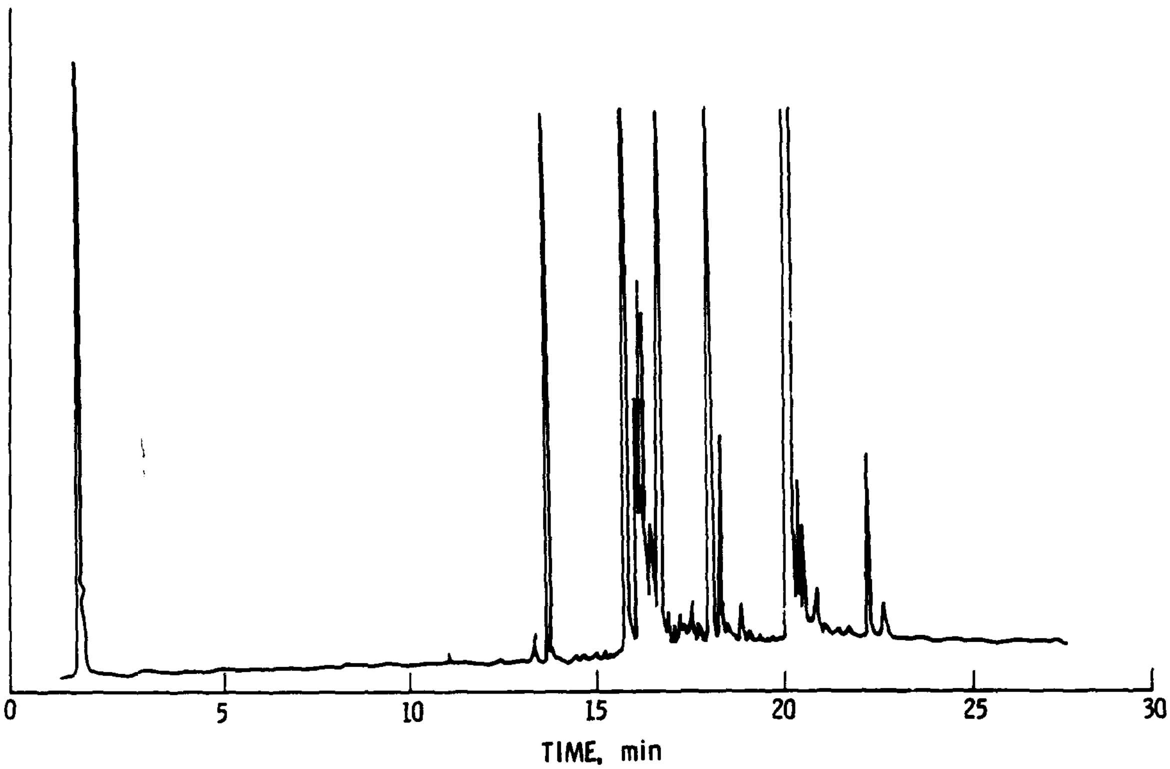

Fig. 5. Gas Chromatogram of Unused Grease-Soap Portion Methyl Esters in Heptane Solvent

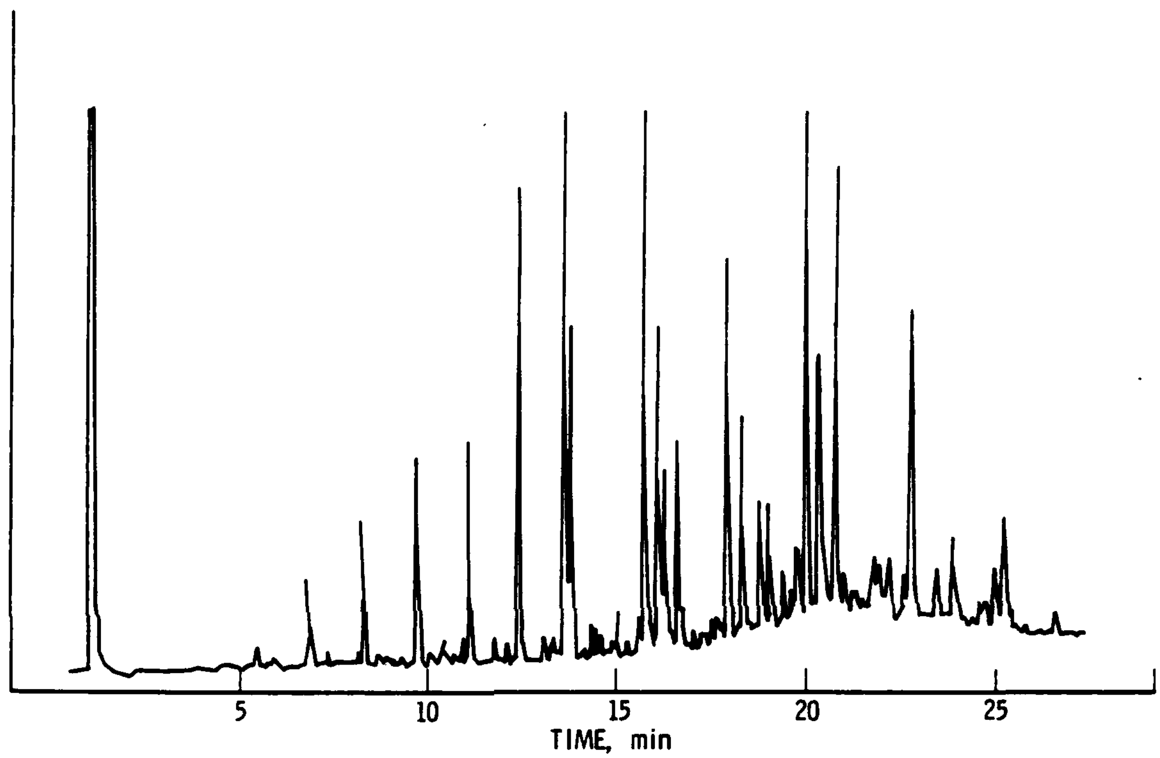

Fig. 6. Gas Chromatogram of LT 1 Soap Portion Methyl Esters in Heptane Solvent

phenyl-β-naphthylamine, and the envelope corresponds to the naphthenic oil. The shape and position of the envelope are essentially the same for the oil fractions from all the samples. There is a slight decrease in the lower molecular weight portions of the used oil chromatograms, indicating some evaporative loss during the tests. No other significant changes in the oil molecular weight distribution occurred. The AT No. 2 and LT oil GC traces (not shown) contain solitary peaks preceding the envelope. These peaks occur at longer retention times than the antioxidant peak and, thus, do not correspond to the antioxidant but rather to some grease degradation products. (The antioxidant is expected to vaporize and leave the grease under vacuum.)

The gas chromatograms for the esterified soap fractions are nearly identical for the unused grease and the AT No. 2 samples (AT GC trace not shown), whereas the GC traces for the LT samples are different. For the unused grease, Fig. 4, the peaks of interest are between retention times 13.62 and 22.19 min. There are five major peaks at RT = 13.62, 15.77, 16.69, 17.97, and 20.14 min, and at least nine smaller peaks that are measurable. The typical LT esterified soap fraction GC trace, Fig. 6, exhibits five significant peaks at retention times less than 13.62 min and several at retention times longer than 22.19 min. In the 13.62 to 22.19 min region, the relative sizes of the peaks changed compared with those of the unused grease, and several new peaks appeared. This result indicates that changes occurred in the grease soap portion for the LT samples.

The changes in the esterified soap fraction component were quantitated as follows: (1) the integrated areas of the five peaks at RT of less than 13.6 min (low RT peaks) and the four peaks at RT = 15.77, 16.69, 17.97, and 20.14 min (high RT peaks) were normalized internally to the area of the peak at 13.62 min. (This peak corresponds to the methyl ester of palmitic acid, a C_{16} saturated fatty acid that does not appear to change in amount from sample to sample.) (2) The normalized low RT peak areas were added together as were the high RT peak areas. The low RT area sums are referred to as the low molecular weight product species sums, whereas the high RT area sums, listed in Table 4, are the reactive species sums. (3) The two sets of values for all the samples are plotted in Fig. 7. There is a strong correlation between the disappearance of the reactive species and the appearance of the product species.

Table 4. Reactive Species vs. Low Molecular Weight Product Species

Sample	Reactive Species Sum	Low Molecular Weight Product Species Sum
1	25.52	0
	24.61[a]	0[a]
2	25.85	0
3	12.37	0.38
4	5.09	2.13
6	15.27	0.49
7	7.70	0.92
8	8.70	1.54
9	19.68	0
11	22.12	0
	29.79[a]	0[a]
12	11.61	0.64
13	13.3	0.18
	20.65[a]	0.56[a]
14	14.14	0.26
	18.53[a]	0.34[a]
16	10.73	1.27
17	1.73	2.19
	2.89[a]	4.50[a]
18	8.38	1.17
	1.13[a]	1.80[a]

[a]Data from GC runs at a later date on the same samples.

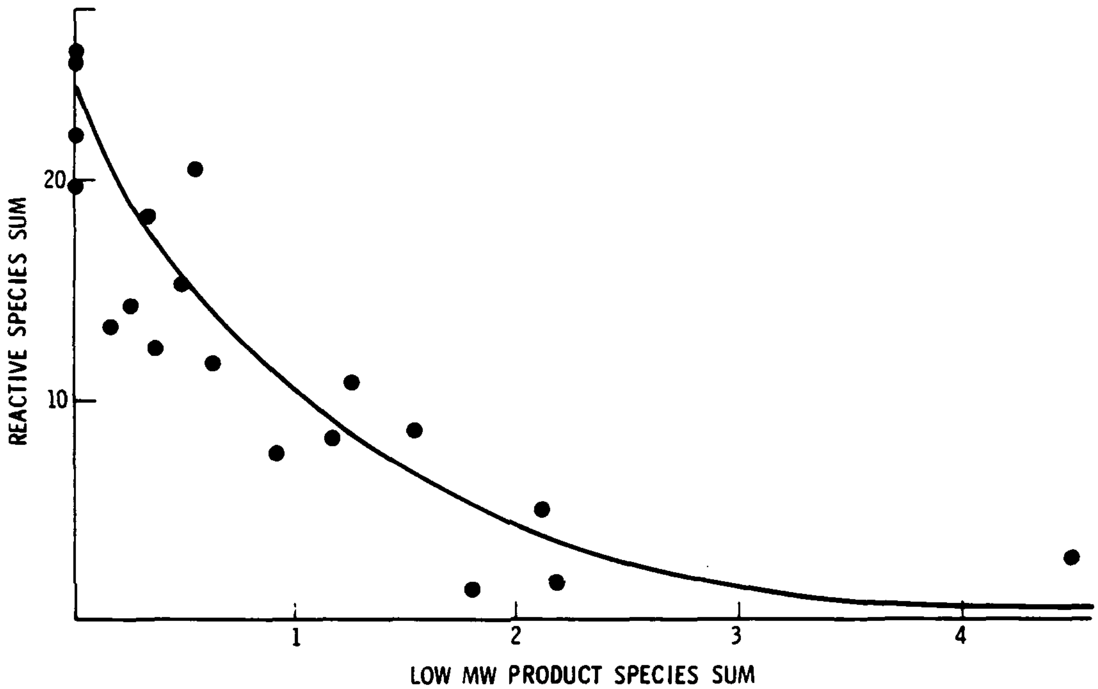

Fig. 7. Soap Oxidative Degradation: Conversion of Soaps to Products

D. GAS CHROMATOGRAPH-MASS SPECTROMETER (GC-MS)

The oil and esterified soap fractions of unused, AT No. 2, and LT greases were analyzed by means of GC-MS.

1. OIL FRACTIONS

The GC trace of the oil from the unused greases exhibited a solitary peak and an envelope. The mass spectrum of the solitary peak (RT = 10.31 in Fig. 5) is consistent with phenyl-β-naphthylamine, a common antioxidant. The oil fractions from the AT and LT samples also exhibited an envelope and a solitary peak in their GC traces. The mass spectra of the solitary peaks are not consistent with phenyl-β-naphthylamine but are consistent with hydrocarbons. Further identification is not possible without more detailed mass spectral data.

2. SOAP FRACTIONS

The mass spectral traces permit us to make the following tentative assignments for the methyl esters in the unused grease shown in Fig. 5: RT = 13.62 methyl palmitate, RT = 15.77 methyl oleate, RT = 16.69 methyl linoleate, RT = 17.97 methyl linolenate, RT = 20.14 methyl ester of a C_{20} polyunsaturated fatty acid. Methyl stearate was identified between methyl oleate and methyl linoleate on the trace. These fatty acid esters are typical of esters derived from soaps used in grease formulations.

Mass spectral data for the LT esterified soap fractions yield the following results: The five significant peaks at RT < 13.69 and the peak at 13.81 (Fig. 6) have the characteristics of a homologous series of unsaturated fatty acid esters, i.e., a series of compounds that increase in chain length by one carbon atom per compound. The compounds that show peaks at RT > 20.14 min include both saturated and unsaturated fatty acid esters. The individual components were not identified.

E. MICROSCOPIC AND XPS ANALYSES OF PARTICLES

The particles that remained following removal of the oil and soaps were definitely translucent under microscopic analysis. XPS analysis indicated that there were no elements other than carbon, oxygen, and sodium on the

surface. Note that XPS sensitivity for hydrogen is approximately four orders of magnitude less than for carbon and oxygen, so although hydrogen is not detected, it is undoubtedly present in the particles. The evidence is consistent with the particles being polymeric without significant quantities of wear metals present. The possibility that the particles are metal fragments that are coated with polymeric material can be ruled out because of the translucent nature of the particles.

F. OBSERVED BEARING DRAG TORQUE VALUES

The rates of increase in the measured bearing drag torque levels for LT No. 1 and LT No. 5 were a minimum of 2.8 times larger than those for the other tests.

4. DISCUSSION

The results of the analyses indicate the following: (1) Very few measurable changes took place in the oil portions of the grease samples compared with the unused grease. (2) The LT samples, but not the AT samples, had oxidized. This degradation was most severe for the samples from LT No. 1 and LT No. 5. (3) Polymeric particles were formed in all the grease samples, which implies that oxidation of the oil and soap might contribute to, but is not required in the observed grease polymerization.

The only noticeable changes in the oil portions of the grease samples when they were compared with the unused grease were the disappearance of the antioxidant phenyl-β-naphthylamine and the appearance of hydrocarbon-like species. The disappearance of the antioxidant is not surprising. It is present primarily to protect the grease from oxidation during exposure to air. Under vacuum conditions, even at the 10^{-4} to 10^{-3} torr level, phenyl-β-naphthylamine is sufficiently volatile to vaporize and leave the grease. The appearance of the solitary, hydrocarbon-like species in the used grease samples cannot be fully explained without more mass spectral data, which would yield molecular weight information. The peak is unusual in that it must result from only one or several closely related species. Thermal or oxidative degradation of the oil or soap would be expected to yield an array of products covering a range of molecular weights. Regardless of the source of these species, they represent only a small fraction of the heptane soluble material in the grease.

There are no major changes in the oil molecular weight distribution between the unused and used greases. Slight differences in the low molecular weight region indicate that evaporative oil loss may have occurred. However, no indication of other degradation mechanisms is apparent in the GC data for the oil portions.

The infrared spectra of the oil fractions indicate that oxidation of the LT samples took place. Aldehydes and ketones are the oxidation products that would be soluble in the oil. However, evidence for these compounds is not

apparent in the GC data, because they would probably be camouflaged by the oil envelope.

Soap degradation, presumably the result of oxidation, is apparent in the LT soap fraction data. The salts of the unsaturated fatty acids (e.g., oleic, linoleic, linolenic) undergo the most change as shown by the GC and GC-MS data for the esterified soaps. New carboxylic acids appear at lower and higher molecular weights. The five lower molecular weight species form a homologous series of C_9 through C_{13} unsaturated fatty acid methyl esters. In addition, C_8 and C_7 unsaturated fatty acid methyl esters appear as minor components in the GC-MS traces. The new species that appear at higher molecular weight could not be identified by means of the GC-MS analysis, although they are methyl esters of carboxylic acids.

The selective disappearance of the unsaturated soap components (especially those that are polyunsaturated) can be explained in a straight-forward manner. Autoxidation occurs by means of a free radical mechanism in which the rates of hydrogen abstraction and concommitant radical formation are dependent upon the structure of the reactant hydrocarbon.[1-4] Olefinic compounds can form resonance-stabilized radicals and, thus, react much faster than saturated hydrocarbons in radical forming reactions. Hence, the unsaturated soaps would oxidize much faster than their saturated analogs.[1,4] (The rate of hydrogen abstraction is rate limiting in these reactions.[3]) This also explains why the palmitic acid soap component, a saturated soap, does not appear to change significantly in concentration. The product distribution can be rationalized by considering that, in unsaturated systems, the radical site can vary over many of the carbon atoms in the molecule because of resonance and double bond isomerizations.[5] The lifetime of the free radical, i.e., the length of time the radical exists before reacting with oxygen (with subsequent cleavage or rearrangement) or with another organic radical (polymerization) can determine whether the radical site has equilibrated. (The oxidation of unsaturated fatty acids has been shown to yield a variety of degradation products.[6-10]) The product distribution indicates that equilibration probably has occurred.

The elevated iron and chromium levels in the samples with the highest level of oxidation (LT No. 1 and LT No. 5) could be the result of wear, interaction of the metal surfaces with oxidized lubricant species, or both. Iron is believed to react with oxidized lubricant and, therefore, can be incorporated into polymeric material during polymerization.[11,12] In addition, metals have been shown to catalyze oxidation of mineral oils, homogeneously, and would be expected to be present in the oil phase of the lubricant.[13] With our data, we cannot distinguish among the possible pathways, although the presence of chromium at a level of approximately 15% of the iron content in the grease (essentially the same percentage as in stainless steel) coupled with the lack of iron in the particles indicates that wear was probably more important than chemical interactions in these systems. If chemical interactions were important, one might expect a difference in selectivity leading to a different percentage of chromium in the grease.

The AT samples exhibited no signs of soap degradation (oxidative or otherwise) in the GC traces, even though significant quantities of polymeric particles were observed in the samples. (It has been shown that the products of lubricant oxidation appear in polymeric sludge.[11]) It is reasonable to assume that the polymerization reactions, such as autoxidation, are free radical and that oxidation and polymerization are competitive. At low oxygen pressures (the overall pressure in the AT tests was 10^{-3} torr, so the oxygen pressure is even less) the oxidation rate expression has the form[3]:

$$\text{rate} = K\,[SH]\,[O_2]$$

where K is a composite rate constant and [SH] and $[O_2]$ are the grease substrate and oxygen concentrations, respectively. The polymerization reaction can occur by means of two concommitant routes: (1) Two radicals can combine, forming one larger molecule. The larger molecule would have to react to form a new radical before undergoing further polymerization. (2) A radical can add to an unsaturated molecule, yielding a higher molecular weight radical. This process is typical of olefinic radical polymerizations. At high temperatures, the radicals can be formed either by hydrogen abstraction or by pyrolytic

carbon-carbon bond cleavage, yielding radicals and olefins that can react as in (1) and (2) or lower molecular weight hydrocarbons that would evaporate from the system. The kinetics of the system would be very complex, i.e., the rate would probably have a substrate concentration dependence of greater than unity:

$$\text{rate} = K\,[SH]^n$$

where $n > 1$. The observations that oxidation had not occurred in the AT samples, that the soap components retained the same relative proportions and did not appear to have degraded, and that polymerization of the grease occurred are difficult to rationalize. Two possible explanations are: (1) Radical formation was nonselective. At high reaction temperatures (generated at asperity contacts), reaction selectivity would decrease (reactivity-selectivity principle) causing radicals to be formed with equal probability regardless of molecular structure. Under these conditions, substrate molecules would retain the same relative proportions. (2) The polymerization occurs by a different mechanism that does not involve free radicals. Neither explanation is satisfactory. For the first explanation to be valid, the temperatures encountered in the AT test would have to be significantly higher than those in the LT test, because at lower temperatures, the unsaturated species would react faster. This does not seem reasonable, because the test conditions were similar. The second explanation is also unreasonable, because chemical intuition would indicate a radical mechanism for the polymerization reactions. The absence of oxidation implies a lack of oxygen at the reaction site. This is also difficult to rationalize, because the tests were all run at the same speed, the test fixtures were similar, and the pressure was higher in the AT test than in the LT tests. With the currently available data, this anomalous behavior cannot be resolved.

The data from Fig. 7, which correlate unsaturated soap disappearance with new product appearance, also correlate with data pertaining to the bearings. The bearings from LT No. 1 and LT No. 5 exhibited raceway cross curvature deviations that were considerably larger than the values for the bearings used

in the other tests. From these results, in conjunction with our chemical analysis results, we conclude that the lubricant degradation (oxidation) is a symptom of adverse mechanical conditions in the bearings rather than the cause of anomalous bearing wear, because lubricant degradation was not as severe in other tests run under identical conditions. In addition, our results indicate that the degradation in the lubricant soap portion can act as an indicator of adverse bearing conditions.

5. CONCLUSIONS

By means of chemical analysis of lubricant samples, it has been shown that oxidation of a naphthenic oil-sodium soap thickened grease can be seen in infrared spectra of the greases and separated components, and also that oxidation degradation is clearly shown in the gas chromatographic traces of the soap methyl ester derivatives. A correlation between the breakdown of unsaturated components and the appearance of lower molecular weight degradation products was also observed. The grease samples that exhibited the highest level of oxidative degradation came from the bearing units that exhibited the highest measured drag torque levels during life testing.

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LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry aerodynamics and heat transfer, propulsion chemistry and fluid mechanics, structural mechanics, flight dynamics; high-temperature thermomechanics, gas kinetics and radiation; research in environmental chemistry and contamination; cw and pulsed chemical laser development including chemical kinetics, spectroscopy, optical resonators and beam pointing, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and bioenvironmental research and monitoring.

Electronics Research Laboratory: Microelectronics, GaAs low-noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter-wave and microwave technology.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; component failure analysis and reliability; fracture mechanics and stress corrosion; evaluation of materials in space environment; materials performance in space transportation systems; analysis of systems vulnerability and survivability in enemy-induced environments.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the upper atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, infrared astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.